8 ORGANIC ANALYSIS, PERFORMANCE QUALITY CONTROL AND ANALYTICAL OPERATIONS

8.1 Introduction

This chapter is a discussion of the analytical operations and procedures used in this laboratory by the Organic Chemistry Section (OCS) to measure and record analytical performance. This chapter is intended to include elements of quality control, introduced in Chapter 5 of this manual, in more detail and provide general guidance for organic analytical chemistry operations. Specific methods and standard operating procedures provide further detail for quality control (QC) requirements and generally take precedence over other guidance.

8.2 Organic Methodology

Various EPA programs including RCRA, CERCLA, NPDES, Drinking Water, Air Toxics, and CERCLA require or recommend the use of specific analytical methods associated with these programs. Organic methods are selected by the analysts in consultation with the appropriate lead analyst and/or section chief based on information provided when the samples are scheduled into the lab. Analytical Standard Operating Procedures (SOPs) for the various methods in use in each laboratory must be placed within the lab for reference purposes. Analysts must be knowledgeable of the SOPs for the determinations which they perform.

8.2.1 Guidance During the course of generating data on samples for organic parameters, it is the policy of the Organic Chemistry Section to 1) apply the best laboratory practices 2) use approved methodology when mandated by regulation and use standardized methodology, if possible 3) when approved methodology is not applicable, fully document all operations associated with the generation of data and 4) meet certain quality requirements that will be designated in the following paragraphs. It should be noted, however, that occasionally certain matrices and samples present analytical challenges, or are not amenable to standardized methodology. In these instances modifications to standard protocols may have to be made to produce a high quality analysis. When this occurs, any deviations from standard operating procedures will be documented.

8.2.1.1 Method Development or Modifications Any new instrumentation installation, development of methods, or major modifications will be performed or guided by Lead Analysts or the Section Chief. At a minimum, verification consists of 1) optimizing instruments and methods to perform analyses within the specific method guidelines or QC guidelines of this quality assurance manual 2) performing a demonstration of capability (DOC) and method detection limit (MDL) and 3) documenting the verification and storage of documentation by the Section Chief. Progression for method development and modifications shall be well documented. The analyst should test matrices and interferences anticipated being relevant to the test method. As a final step, the analyst shall develop a standard operating procedure consistent with the format used by the ASB. When the method has appropriate approval, a memo will be issued by the analyst to the Section Chief concerning the date of implementation of the new method and any other pertinent information.

8.2.2 Safety - Safety precautions associated with the safe handling of toxic chemicals, reagents, solutions and samples will be observed and regarded as a first order responsibility of the analyst. The analyst will take the necessary precautions to prevent exposure or harm both to self and co-workers.

8.2.3 Water - Water used to prepare calibration standards, spike solutions, standard reference solutions or any sample dilutions or mixtures must meet or exceed the requirements for Type I grade water as specified by the American Society for Testing and Materials (ASTM); Standard Practice D 1193. This grade water is equivalent to Type I water as specified in Standard Methods 1080. The parameter measured to verify the quality of water is resistivity, with a requirement of 18 megohm-cm at 25°C or better. See also section 2.2 of "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," (EPA 600/4-79-019, March l979), and any future updates of the manual. For volatiles analysis, reagent water may be prepared by heating at 80°C and purging with ultra high purity helium.

8.2.4 Reagents and Standards - Reagents must be ACS reagent grade quality or better. Reagents and standards will be dated upon receipt and will be properly disposed of when the shelf life has been reached (see Chapter 4). Working solutions and mixtures made from stock reagents and standards will be used only for the appropriate working life of the solution.

8.2.5 Records of Repair and Maintenance Records for the repair and maintenance of instruments shall be maintained within the Section. The preference is to keep these records with the instrument in a bound log and for the working life of the instrument.

8.3 <u>Reviewing/Verification/Recording</u>

8.3.1 All analytical results for reporting will be reviewed/verified by another analyst familiar with the analysis. The primary analyst shall to the best of his/her ability correct all mistakes and resolve all questionable issues before the results are submitted for verification. The review should at a minimum check to see that all required documentation is included with the raw data, proper QC protocols were followed, documentation of any excursions from analysis requirements (e.g., QC acceptability, method, etc.), and a check for math errors. The check for math errors may be from minimal (for routine analyses, a check of one or more calculations) to 100% verification at the discretion of the reviewer. Verification of the data shall be recorded (date and initials of the reviewer) and it is strongly encouraged that the reviewers either fill out a checklist of items reviewed or indicate with initials/date which items were verified. The checklist is the preference. Additionally, the Section Chief may perform spot checks of raw data on randomly selected projects. These spot checks are documented on a checklist and filed with the raw data in the project file.

8.4 General QC

8.4.1 Guidance Quality control results are used for making decisions about analyses. Analysts have guidelines available for accepting, rejecting, and flagging results. These include, but are not limited to acceptance limits based on method requirements or historical data, guidelines developed in-house for the area of interest, and method specific guidelines. Method guidance generally takes precedence over other guidance.

8.4.2 Special Circumstances Occasionally, the primary analyst will encounter a situation that is not addressed by available guidelines. The analyst should consult the Lead Analyst or Section Chief in these cases. When possible, decisions will be based on the data quality objectives (DQOs) of the project. For example, if while performing duplicate analyses one result is above the MQL and the other is below (but above the MDL), it may be determined that the MQL is well below the regulatory level or study level of concern and thus the average of the two results will be reported. If study requirements determine that results at the MQL are of importance, the primary analyst may be required to rerun the analyses to clarify or confirm the results.

8.4.3 Demonstration of Capability (DOC) Before a new method may be used for sample analysis, a DOC must be performed according to the method or any requirements set forth in Chapter 5. Method guidelines may be used if the requirements of Chapter 5 are also met.

8.4.4 Holding Times

8.4.4.1 Holding times begin when the sample is taken. The OCS has chosen to follow the recommendation that holding time starts at the end of the composite period for composite samples. See Appendix to this Chapter - Data Review for Organic Analyses for additional guidance.

8.5 Method Blanks

8.5.1 Method Blank Objective

8.5.1.1 A method blank is defined as a sample of a matrix similar to the batch of associated samples (when available) that is (1) free from the analytes of interest, (2) processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures and (3) free of target analytes or interferences at concentrations that impact the analytical results for sample analyses. ASB uses the results of the method blank analysis to assess potential contamination of the associated sample batch.

8.5.2 Method Blank Procedure - Semivolatiles and Pesticide/PCBs

8.5.2.1 When an extraction is performed or when chemical waste samples are prepared by dissolution in a solvent, a method blank is prepared with every batch (i.e. samples prepared on the same day) and matrix type consisting of 20 samples or less. When processing the method blank, include all glassware and extraction equipment which are normally used in the sample preparation.

8.5.2.1.1 Water sample blank - Use reagent grade water and all solvents.

8.5.2.1.2 Soil/Sediment/Tissue sample blank - Use the appropriate amount of anhydrous sodium sulfate or hydromatrix and all solvents and reagents as added to samples. This would include anhydrous sodium sulfate added to semivolatiles.. Analyte free sand is the material of choice for soil/sediment blanks.

8.5.2.1.3 Waste and Air sample blanks- Use all solvents and reagents as added to samples.

8.5.3 Method Blank - Evaluation Criteria and Corrective Action

The Lead Analyst shall use professional judgement and the guidance listed in this section to determine if the sample(s) associated with a contaminated blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes when Method Blank results are outside acceptance criteria. In all cases the course chosen shall be documented. See Appendix to this Chapter - Data Review for Organic Analyses for additional guidance.

8.6 Laboratory Control Samples (LCS)

8.6.1 LCS Objective

A Laboratory Control Sample (LCS) is defined as a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards, or a material containing known and verified amounts of analytes. The LCS is generally used to establish intra-laboratory or analyst specific precision and bias, or to assess the performance of all or a portion of the measurement system. ASB uses the LCS as a “best case” indicator of the overall performance of the analytical system.. See Appendix to this Chapter - Data Review for Organic Analyses for additional guidance.

8.6.2 LCS Procedure

LCS spikes may be prepared using reference materials (including performance evaluation or proficiency testing samples) or internally-prepared spiking mixtures. Clean matrices such as reagent grade water and sand are used to provide consistency for determining system performance. The LCS is to be carried through the entire analytical process. Note that an LCS duplicate will routinely be prepared and analyzed to provide data for the evaluation of analytical precision. See Appendix to this Chapter - Data Review for Organic Analyses for additional guidance.

8.6.2.1 Volatile Organic Compounds

Volatile organic analysis (VOA) by Purge and Trap/GC/MS is a unique case in which the standards are analyzed through the entire analytical process. In essence, each time a continuing calibration standard is analyzed it represents an "LCS" since the preparation and analysis steps are included in each and every calibration run. For purposes of meeting the LCS requirements for VOA the following steps shall be taken:

8.6.2.1.1 At the beginning of each work week, along with the routine continuing calibration standard, analyze a reference standard from an external source. This shall serve a dual purpose as the LCS control and to verify the routine calibration standard with an external reference.

8.6.3 LCS - Evaluation Criteria and Corrective Action

8.6.3.1 The LCS is to be carried through the entire analytical process. Control limits should be initially established after at least 20 separate spikes have been performed and shall be matrix and method specific. If the analytical method provides directions for calculating LCS limits, then follow the method specified procedure, otherwise acceptance limits shall be calculated representing 3 standard deviations from the mean recovery for each compound. See Appendix to this Chapter - Data Review for Organic Analyses for additional guidance.

8.6.3.2 New LCS limits must be generated each time a new method is implemented, when significant changes are made to existing methods, or if the spiked components are changed,

8.6.3.3 In the absence of current acceptance limits use as guidance the best available estimation of limits from established methods or other sources. Judgements on data quality (i.e., adding qualifier flags, etc.) will not be made solely on the basis of these estimated limits until such time as acceptance limits are appropriately determined. In these instances consult the Section Chief and Branch QAO for guidance

8.7 <u>Surrogates</u>

8.7.1 Surrogates - Objective

8.7.1.1 A surrogate standard is defined as a compound which behaves similarly to one or more target analytes and is not expected to occur in an environmental sample. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated by determining whether the measured concentration falls within the statistical acceptance limits. Sample results with surrogate limits that fall outside acceptance criteria are qualified appropriately. See Appendix to this Chapter - Data Review for Organic Analyses for additional guidance.

8.7.2 Surrogate Procedure

8.7.2.1 Surrogate standards are added to each sample (including blanks and the LCS) just prior to sample preparation, i.e., extraction or purging. Following are the surrogate standards and the corresponding spike solution concentrations currently used by ASB:

Semivolatile-Base/Neutral	**Sol'n Conc.**	**Spike Vol. /Final Extract Vol.**
Nitrobenzene - d5	1000ng/uL	50uL/1mL
Terphenyl - d14	1000ng/uL	
Semivolatile-Acid	**Sol'n Conc.**	**Spike Vol./ Final Extract Vol**
2,4,6-tribromophenol	1000ng/uL	50uL/1mL
phenol - d6	1000ng/uL	
Volatiles-Water/Soil/Sed	**Sol'n Conc.**	**Spike Amt/Final Purge Vol.**
toluene - d8	Method 8260	Method 8260
p-bromofluorobenzene	modifications	modifications
dibromofluoromethane		
Volatiles-Air Canister	**Sol'n Conc.**	**Spike Amt/Final Canister Vol.**
toluene - d8	TO- 15	TO- 15
p-bromofluorobenzene	modifications	modifications
dibromofluoromethane		
Organo-chlorine Pesticides and PCBs	**Sol'n Conc.**	**Spike Vol./ Final Extract Vol.**
2,4,5,6 tetrachloro-meta-xylene (TCMX)	20ng/uL	25uL/1mL
decachlorobiphenyl (DCBP)	40ng/uL	25 uL/1mL
Phenoxy Herbicides	**Sol'n Conc.**	**Spike Vol./ Final Extract Vol.**
2,4 -Dichlorophenyl-Acetic Acid (DCAA)	20ng/uL	100uL/10mL

Organonitrogen/phosphate Pesticide	**Sol'n Conc.**	**Spike Vol./ Final ExtractVol.**
2-Nitro-m-xylene (NMX)	250ng/uL	50uL/1mL

8.7.2.2 Analysis of Surrogates

8.7.2.2.1 Volatile and Semivolatile Organic Compounds - All samples and blanks are to be analyzed by GC/MS. The GC/MS analyst is responsible for calculating recovery, recording the data in the GC/MS logbook and transferring it to the data base using appropriate software.

8.7.2.2.2 Pesticides/PCBs - Most samples and blanks will be analyzed by GC/EC or GC/NP for pesticides/PCBs. The analyst is responsible for keeping a hardcopy of the pesticide surrogate data in the project file as well as transferring the data to the computer data system.

$$\text{Percent Surrogate Recovery} = \frac{Qd \times 100}{Qa}$$

Where Qd = Quantity determined by analysis
Qa = Quantity added to the sample

8.7.3 Surrogates - Evaluation Criteria and Corrective Action

8.7.3.1 Surrogate Acceptance Limits

8.7.3.1.1 Surrogate acceptance limits are calculated yearly based on data generated in samples for the previous two years. Calculate average recovery (%R) and standard deviation (S), in percent recovery, for each surrogate standard using the entire data base.

8.7.3.1.1.1 Only results from sample analyses are maintained in the database. (Note: blank and LCS results are not to be used in the calculation of limits).

8.7.3.1.1.2 Obvious outliers are not entered into the surrogate database based on the analysts judgement on a case by case basis (i.e. dilutions beyond quantitation range, obvious spiking errors, interference, etc.). Surrogate results from samples exceeding existing limits are only entered into the database when repeat analysis confirm those results.

8.7.3.1.2 Limits are established as follows:

8.7.3.1.2.1 Database outliers are established by summarizing all the data in the database then applying one standard deviation beyond that used to determine the limits for the specific analysis.

8.7.3.1.2.2 Limits are then recalculated based on the remainder of the data. For example: assuming the final limits are set using 3 standard deviations. A standard deviation calculation is made of the entire database, then a new calculation is made eliminating all data exceeding 4 times the standard deviation from the entire database.

8.7.3.1.3 New surrogate limits must be generated each time a new method is implemented, when significant changes are made to existing methods, or if the spiked components are changed.

8.7.3.1.4 In the absence of current acceptance limits use as guidance the best available estimation of limits from established methods or other sources. Judgements on data quality (i.e., adding qualifier flags, etc.) will not be made solely on the basis of these estimated limits until such time as acceptance limits are appropriately determined. In these instances consult the Section Chief and Branch QAO for guidance. See Appendix to this Chapter - Data Review for Organic Analyses for additional guidance.

8.7.3.2 Guidance for Reporting Contaminants - General Criteria

8.7.3.2.1 Surrogates outside the acceptance criteria must be evaluated for the effect indicated for the individuals sample results. The appropriate corrective action will be determined by the Lead Analyst exercising professional judgement while considering data quality objectives or other site specific requirements.

8.7.3.2.2 Check for instrumental problems and make any necessary corrections. Redilute the extract (if necessary), and then rerun the sample. This also applies to blanks and matrix or LCS spikes.

8.7.3.2.3 If no instrumental problems exist, the sample should be re-extracted and re-analyzed. However, if project requirements (e.g. turn around times) dictate that sample data from the first analysis must be reported, report that data with a "J" flag.

8.7.3.2.4 If the surrogates are still outside the acceptance limits after re-analysis, the data will typically be reported and flagged with a "J". Notably, there may be certain instances for which more work is warranted for special project needs.

8.7.4 Recording Surrogate Data

8.7.4.1 All surrogate data must be transferred to the computer data system except for surrogates in blanks and surrogate data that is known to be in error; e.g.., acid was not added to water prior to water extraction, valve on GPC instrument was leaking causing cross-contamination, purge and trap system contamination, etc.

There must be clear documentation in the data as to why a particular surrogate value was not added to the database.

8.8 Matrix Spikes

8.8.1 Matrix Spike - Objective

8.8.1.1 A matrix spike (MS) is defined as a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent measurement of target analyte concentration is available . ASB uses matrix spikes to assess the effect of a particular sample matrix on the recovery of target analytes spiked into that specific sample only. Matrix Spikes are generally not prepared by the Organic Chemistry Section unless requested by the Project Leader to meet site specific DQOs.

8.8.2 Matrix Spikes - Procedure

8.8.2.1 The frequency of the analysis of matrix spike samples shall be determined as part of the systematic planning process (e.g. Data Quality Objectives) or as specified by the required mandated test method. Replicate analyses are usually part of MDL/DOC studies, recovery studies, or in method development studies.

8.9 Laboratory Duplicate Matrix Analyses

8.9.1 The frequency of the analysis of matrix duplicates may be determined as part of a systematic planning process (e.g. Data Quality Objectives) or as specified by the mandated test method.

8.9.2 The results from matrix duplicates are primarily designed to assess the precision of analytical results in a given matrix. Results are compared to the acceptance criteria as published in the mandated test method internally established limits.

8.10 Internal Standards

8.10.1 Internal standards are compounds not expected to occur in environmental samples which are added to each sample just prior to instrumental analysis. ASB uses internal standards to evaluate instrument performance and in the quantitation of target analytes for GC/MS analyses. GC/MS analysts are responsible for selecting the appropriate internal standards based on the analytical method requirements. See Appendix to this Chapter for guidance on the evaluation of internal standards results.

8.10.2 Following are the internal standards and the corresponding spike solution concentrations currently used by ASB:

Semivolatile	Sol'n Conc.	Spike Volume per Final Extract Volume
1,4-Dichlorobenzene-d4	1000ng/uL	10uL/1mL
Naphthalene-d8	1000ng/uL	10uL/1 mL
Acenaphthene-d10	1000ng/uL	10uL/1 mL
Phenanthrene-d10	1000ng/uL	10uL/1 mL
Chrysene-d12	1000ng/uL	10uL/1 mL
Perylene-d12	1000ng/uL	10uL/1 mL

Volatiles-Water/Soil/Sed	Sol'n Conc.	Spike Volume Per Final Volume
1,4-Difluorobenzene	Method 8260	Method 8260
Chlorobenzene-d5	modifications	modifications
1,4-Dichlorobenzene-d4		

Volatiles-Air Canister	Sol'n Conc.	Spike Volume Per Final Volume
Difluorobenzene	TO-15	TO-15
Chlorobenzene-d5	modifications	modifications
1,4-Dichlorobenzene-d4		

8.11 Data Reporting

8.11.1 General Reporting Conventions

All analytical data generated in the Branch will be entered into and reported from the Region 4 Laboratory Information Management System (R4LIMS).

8.11.1.1 The primary analyst is responsible for entering and proofing the data. The Lead Analyst is responsible for verifying the results. If the Lead Analyst is not available the primary analyst will verify the results.

8.11.1.2 The Lead Analyst is responsible for producing a verified copy of the results for the customer and a copy for the project file. Other copies will be produced as needed. A memo transmitting these results will be generated from R4LIMS and signed at the time of production by the analyst that report the results. This memo will also explain any anomalies in the results.

8.11.1.3 The Section Chief or an alternate in the Section Chief's absence will review the production copies and memo for completeness and accuracy. The Section Chief signs the transmittal memo, Branch Releases the data in R4LIMS, and forwards the data to the Branch Secretary for appropriate routing.

8.11.1.4 In the event a correction or change needs to be made in data that has been Branch released and transmitted to the customer the Section Chief is responsible for insuring corrected data is produced and transmitted to the customer. A new memo should be created from R4LIMS transmitting the corrected data, describing the changes, and instructing the customer to replace the previously reported data with the corrected data. This is achieved by reversing the above procedure and starting the process over.

8.11.1.5 No data will be reported until all QC data has been evaluated and the data are verified.

8.11.1.6 All soil, sediment, waste and tissue data must include a remark indicating whether the data are reported on a wet weight or dry weight basis.

8.11.1.7 Verify correct concentration in units as specified in R4LIMS for the matrix type.

8.11.1.8 When reporting total constituents (e.g., total DDT residue), J the total concentration if the J values for individual constituents are $\geq$10% of the total value.

8.11.1.9 When reporting estimated minimum quantitation limits (MQL), the MQL is reported to 2 significant figures.

8.11.1.10 Reporting target compounds below the MQL - Report the actual calculated value (to 2 significant figures) with a J for any concentration below the MQL.

8.11.1.11 If dilutions of the sample extract are required, the MQL is raised by the same factor as the dilution.

8.11.1.12 Determine from the analytical request if a specific limit of quantitation is required. This is especially important when analyzing samples for compliance monitoring, spill investigations, and drinking water investigations.

8.11.1.13 Calculate the MQL for the blank using the lowest sample weight or sample volume.

8.11.1.14 Report all non-target (library search compounds) data to 1 significant figure.

8.11.1.15 Inorganic compounds - Do not report sulfur, H_2S, SO_2, etc, identified during GC/MS analysis.

8.11.1.16 Reporting duplicate data - Calculate and report the average with an A flag. If a compound is detected on one duplicate and not the other, do not report the compound.

8.12 Extraction Protocols

8.12.1 General Procedures

8.12.1.1 All glassware and glass wool is rinsed sequentially with methanol, acetone, and the sample solvent, just prior to use. All compatible glassware used for low level analyses will be baked in a drying oven (if available) at the appropriate temperature.

8.12.1.2 Sediment/Soil - Percent moisture must be determined on all samples unless otherwise specified by the sample requestor. All soil/sediment samples shall be reported on a dry weight basis. Non-aqueous waste and tissue samples are reported on a wet weight basis.

8.12.1.3 Chlorinated water samples must be dechlorinated with 10% sodium thiosulfate prior to extraction.

8.12.1.4 The lead analyst for extractions, in consultation with the pesticide and semivolatile lead analysts, will select the appropriate clean-up procedures based on matrix type, required quantitation limit, and known or suspected interferences.

8.12.1.5 If the final extract volume is greater than l mL, transfer at least l mL to a GC vial. The remainder is discarded. Never leave any extracts in volumetric flasks.

8.12.2 Extraction Logbook

8.12.2.1 All pertinent information requested on the sheet will be properly recorded prior to submittal to the GC and or GC/MS chemists. The extraction chemists will also start the Extraction Laboratory Sample Preparation Report and forward it with each batch to the analytical work unit.

8.12.2.2 All logbook pages and forms can be found on the Region 4 SESD's local network drive (K: drive) in appropriate subdirectories of K:\ASB\Forms\ .

8.12.2.3 List the method blank and matrix spike in the sample number column. Record the Batch ID number that relates that blank and spike.

8.12.2.4 Record the extract volume on the sheet.

8.12.2.5 Record the analytical method ID from the Method Tracker.

8.12.2.6 Record unusual occurrences during sample preparation, e.g., unusual appearance of sample, problems during extraction, losses of extract, precipitation and/or increase in viscosity during final evaporation in the logbook.

8.12.2.7 All calculations must be checked by the secondary analyst and the extraction sheet initialed by both primary and secondary analysts.

8.12.2.8 Do not erase or use "Liquid Paper" to correct any error. Put one line through the error with analyst initials and date.

8.12.3 Labeling Laboratory Sample Containers

8.12.3.1 One of the analytical method numbers should be recorded on the sample vial and in the extraction logbook.

8.12.3.2 Record on the blank, spikes, and surrogate included with the sample batch the inclusive numbers of the samples that were extracted together. Use the following designations:

8.12.3.2.1 Blank, Batch ID number, Method Tracker Number, and final volume.

8.12.3.2.2 Sample number and spike, Method Tracker Number, and final volume.

8.12.3.2.3 “X” and “Y” - To designate duplicates including LCS and LCSD extractions.

8.12.3.2.4 “R”, “R2", “R3", etc. - To designate when re-extractions are required; designate them with an "RX" depending on the number of re-extractions required.

8.12.3.2.5 A mark is placed on each sample vial to indicate the bottom of the meniscus when vialed.

8.12.3.2.6 The final extract volume is recorded on all vials and in the extraction logbook.

8.12.4 Sample Vial Handling

8.12.4.1 Put all vials on one board or container for each batch of samples that were extracted together, and label the board or container with the projects’ names. The chemist in charge of the extraction laboratory should check the labeling of all vials. Do not put two separate extraction batches on one board or in one container.

8.12.4.2 Sample vials and copies of the extraction sheet and Batch Report should be given to the chemist in charge of the pesticide or semivolatile analysis.

8.12.4.3 Include an LCS/Matrix Spike standard solution and a surrogate standard solution with each set of samples. These solutions should be at the same concentration as in the sample extracts. This LCS/Matrix Spike and surrogate standard solution are used by the instrumental analysts to evaluate the recovery of the LCS, Matrix Spike and surrogates in the samples.

8.13 GC Analysis - Pesticides/PCBs

8.13.1 GC Screening - Pesticides/PCBs

8.13.1.1 For some samples, a GC screening may be necessary before the GC analytical run. The option of whether to screen GC samples is left to the analyst's discretion based upon information which is available at the time of analysis. Screening is normally used for waste samples or environmental samples expected to contain high concentrations of analytes. The following set-up is an example for screening all types of matrices.

8.13.1.1.1 Begin the analytical sequence with a GC Performance Mix and prepare a 100x dilution of the surrogate standard or the dilution that is required for the surrogate to be within the standard curve range.

8.13.1.1.2 Prepare a 100X dilution of all extracts and run them sequentially. Include the blank and spike in the sequence. Include a calibration standard and a GC Performance Mix after each 20 samples.

8.13.1.1.3 Repeat the 100X dilution of the surrogate standard at the end of the screening run.

8.13.1.1.4 This run of 100X dilutions may be used to calculate the surrogate recovery if the following procedures were done:

8.13.1.1.4.1 A GC Performance Mix is run both at the beginning and at the end of the run and meets the percent breakdown criteria.

8.13.1.1.4.2 Multiple dilutions of the surrogate standard are run before or immediately after the screening run to determine if the instrument response is linear.

8.13.2 GC Logbook - Pesticides/PCBs

8.13.2.1 Be sure all pertinent information requested on the logbook sheet is properly recorded. The Lead Analyst should keep track of projects on a GC master log sheet.

8.13.2.2 All logbook pages and forms can be found on the Region 4 SESD's local network drive (K: drive) in appropriate subdirectories of K:\ASB\Forms\ .

8.13.2.3 All analysts that participated in making dilutions and/ or loading the auto-sampler must record their names. This includes analysts that add sample extracts at the end of the run to verify or check on samples from other sets of samples.

8.13.2.4 Record inclusive sample numbers associated with each blank and spike.

8.13.2.5 Record the concentration level and the identification code of the analytical standard.

8.13.2.6 Record all information that is needed to identify the sample vial.

8.13.2.7 Record all dilutions with dilution factor, times sign, and original volume (example: 10 X 1 mL or 10,000 X of 25 mL).

8.13.2.8 A copy of the logbook page should be kept in the project file.

8.13.3 Analytical Sequence - Pesticides/PCBs

8.13.3.1 Follow the procedure specified by the quantitation software supplier for setting up instruments for collecting, processing, analyzing, and reporting data. Make sure that the correct time and date are on all QC runs and reports. This can be done by making sure that the processing computer and the acquiring GC are set to the correct time and date.

8.13.3.2 Build a new method, or edit an existing one that is suitable for the analysis as required by the software program being used. This will include developing or updating the instrument, processing and calibrating parameters for the method.

8.13.3.3 Create or edit a report format for the method.

8.13.3.4 Create a new sequence file or edit an existing sequence file for each GC run. The sequence should include information to identify the sample, vial, and method used. Give the sequence file an associated project file name.

8.13.3.5 Download a sequence or method file to the interface.

8.13.3.6 Set the GC conditions for the run and then start the GC to begin data collection.

8.13.3.7 After collection, process the data using a pesticide analysis software protocol.

8.13.3.8 Build summary reports for linear calibration curve, surrogate, spikes (LCS and matrix), % recovery, performance check standard results, continuous calibration verification (CCV) results, and sample results.

8.13.3.9 Archive and back up all files associated with an analytical run on a CD- R or other electronic storage media

8.13.4 Sample Vials- Pesticides/PCBs

8.13.4.1 The GC chemist is responsible for all sample extract vials received from the extraction lab. The chemist is responsible for the vials until the GC analysis is complete and the vials have been stored in proper order until they may be discarded.

8.13.4.2 Re-mark all vials at the meniscus after dilutions or GC analysis. Do not allow original extract vials to remain in auto-samplers over night

8.13.5 Retention Time (RT) Windows- Pesticides/PCBs

8.13.5.1 Retention time windows are extremely important for the qualitative identification of pesticides, however all information available should be used to make pesticide identifications. The experience of the analyst should weigh heavily in the interpretation of chromatograms provided the analyst has the necessary experience in pesticide residue analysis. For multi-response pesticides/PCBs, the analyst should utilize the retention time window but should primarily rely on pattern recognition.

8.13.5.2 For determining retention time (RT) window size for pesticide/PCB analysis, ASB assigns a standard deviation of 0, resulting in a default standard deviation of 0.01 minute as described in SW-846, Method 8000B, section 7.6.3. Therefore the width of the window (3x the SD) will be 0.03 minutes.(Method 8000B, section 7.6.4). If the GC in use cannot meet the 0.03 minute RT window for a particular compound, the following procedures will be followed:

8.13.5.2.1 Three times the standard deviation of the retention time for each pesticide/PCB will be used to establish the retention time window.

8.13.5.2.2 Make a minimum of 1 injection of the compound at 24-hour intervals throughout the course of a 120-hour (5 day) period.

8.13.5.2.3 Calculate the standard deviation of five absolute retention times for each single component pesticide over the 120 day time period. For multi-response pesticides/PCBs, choose one major peak from the group of peaks and calculate the standard deviation of the retention time of that peak. Multiply the SD times 3 to establish the RT window for the compound.

8.13.6 Calibration - Pesticides/PCBs

8.13.6.1 The gas chromatographic system should be calibrated using the external standard technique for all columns used for quantitation whenever a major instrument modification is performed (e.g., new column is installed, detector replaced, etc.) or whenever the continuing calibration verification (CCV) standard does not meet acceptance criteria.

8.13.6.2 Prepare calibration standards at 5 concentration levels with a minimum of 3 for each compound of interest . However, for multi-peak compounds (e.g. technical chlordane, toxaphene, and the aroclors) a single concentration within $\pm$ 20 percent of the sample amount may be used. The lowest standard on the curve shall correspond to the minimum quantitation limit and the highest standard defines the upper boundary of the linear working range. A calibration curve should be established on each GC quantitation column, each new instrument, and whenever the most recent continuing calibration verification standard falls outside of accepted criteria.

8.13.6.2.1 Using injections of 1 to 5 uL of each calibration standard, calculate the calibration factor (CF) for each compound using the following formula:

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}^{*}}{\text{Mass of the Compound Injected (in nanograms)}}$$

* For multi-response pesticides/PCBs use the response of the major peaks used for quantitation

The results are used to prepare a calibration curve for each compound.

8.13.6.2.2 If the run is for confirmation (no quantitation) or to determine MQLs, the linearity check is not required. To determine MQLs, however, a calibration standard at the MQL level of standard QC-1 is required. In addition a continuing verification standard must be within $\pm$15% difference or the response factor must be increasing (e.g. greater than 15% difference).

8.13.6.2.3 Linearity check - Calculate the %RSD on the target compounds as follows: Determine the calibration factor for each concentration by dividing the area or peak height by the amount injected. Calculate the standard deviations (s) of the calibration factors using:

$$S = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}}$$

and then %RSD:

$$\%\text{Relative Standard Deviation} = \frac{s\ (100)}{\text{Mean CF}}$$

If the %RSD is less than or equal (≤) 20 %RSD for the compound the instrument response is assumed to be linear. When any compound is greater than 20% RSD, take the average %RSD of all target compounds. If the average %RSD is ≤ 20% RSD, the calibration instrument passes the linearity criteria. See SW-846, 8000B, section 7.5.

8.13.6.2.4 If the linearity criteria is exceeded perform appropriate maintenance.

8.13.6.2.5 The %RSD may be calculated using 3, 4, or 5 concentration levels depending on the number of calibration standards used for the initial calibration. However, any peaks within the sample quantitated must fall within the selected concentration range.

8.13.6.2.6 The calculation for %RSD for the compounds must be included in the chromatogram package.

8.13.6.3 For non routine analytes or special requests, in consultation with the project leader, it is permissible to calibrate the instrument with one calibration standard. The non-routine analyte may be quantitated against the one point calibration. Data points derived from a one point calibration must be reported as an estimated quantitation with the “J” flag assigned to the reported concentration. These types of calibrations must not be performed independently by the analyst, but shall only be performed after confirmation from the project leader that a single point calibration will meet the project data quality objectives. Documentation of the project leader’s acceptance of this type of data should be added to the project file. However, a single point calibration may be used with no data flags for multi component analytes. See Method 8081A, section 7.4.1.1

8.13.7 Daily GC Column Performance Check- Pesticides/PCBs

8.13.7.1 As a guideline, adjust the carrier flow rate or head pressure and oven temperature so that the standards will be eluted within 30 minutes on capillary columns.

8.13.7.2 Inject a GC/EC column performance (breakdown) mix for organochlorine analyses consisting of:

	ng/uL
lindane	0.010

aldrin	0.010
endrin	0.025
p,p'-DDT	0.030

at the beginning of each run and after each set of 20 samples but no less than every 12 hours. Lindane and aldrin are present in this mixture to monitor instrument performance for early eluting compounds, but are not used to measure breakdown. Calculate the percent breakdown (BD) as follows:

$$\%\ BD\ for\ 4,4'\text{-}DDT = \frac{\text{Total DDT degradation peak area (DDE + DDD) x 100}}{\text{Total DDT peak area (DDT + DDE + DDD)}}$$

$$\%\ BD\ for\ Endrin = \frac{\text{Total Endrin degradation peak areas (E. Ald. + E. Ketone) x 100}}{\text{Total Endrin Peak Area (Endrin + E. Aldehyde + E. Ketone)}}$$

See suggested maintenance section if degradation exceeds 20% for DDT or endrin.

8.13.7.3 All calculations for percent breakdown must be included in the data package.

8.13.8 Continuing Calibration Verification

8.13.8.1 For calibration verification, all target analytes must be injected at a frequency of every 20 samples or after 12 hours, whichever comes first with the following exception: for sites that require PCB analysis, include only the Aroclors that are expected to be found based on site or project knowledge. If PCBs are required but it is unknown which Aroclors may be present, the mid-concentration Aroclors 1242/1260 mixture only need be injected. However, if specific Aroclors are found during the initial screening, it is required that the samples containing Aroclors be reinjected with the proper mid-concentration Aroclor standards.

8.13.8.2 It is recommended that once the 20 sample/12 hour calibration verification requirement has been met, a standard be included after approximately every 10 samples to minimize the number of repeat injections in the event of the failure to meet acceptancelimits. Regardless of the frequency of the interspersion of standards, all target analytes must be analyzed for verification after 20 samples or after 12 hours, whichever comes first. The calibration factor of a specific standard compound shall not exceed a 20% difference from the initial response when screening samples or more than (+/-) 15% difference for any standard used for quantitating. When one or more of the compounds are greater than +/- 15% difference, take the average % difference of all compounds in the standard mix. If the average % difference of all compounds in the standard mix is less than +/- 15%, the calibration verification is considered acceptable. See SW-846, 8000B, section 7.7

$$\text{Percent Difference} = \frac{R1-R2}{R1} \times 100$$

Where R1 = Calibration Factor from first analysis and
R2 = Calibration Factor from succeeding analysis.

8.13.8.2.1 All calculations for percent difference must be included in the data package.

8.13.8.3 Check retention time windows of the continuing calibration verification standard and compare it to the standard run at the beginning of the 12 hour shift . If retention time is outside of calibrated window (+/- .03min or 3 standard deviations) check the GC for problems (i.e., septum and/or column leaks, bad syringe, etc.). However, the experience of the analyst should be considered when making a decision to accept or reject the presence of a compound based on retention time.

8.13.8.4 Check for peak tailing and take corrective action if necessary.

8.13.8.5 If the calibration verification fails acceptance criteria the system should be evaluated in an effort to resolve the problem. All samples following the last acceptable standard must be reinjected.

8.13.8.6 However, if a multi-component analyte (Aroclor, technical chlordane, and toxaphene) falls outside the retention time window criteria but the peak pattern remains valid, the analytical run for those compounds may be used for analysis.

8.13.9 Suggested Maintenance- Pesticides/PCBs

8.13.9.1 Corrective measures to address compound degradation, inadequate resolution, and/or peak tailing may require any one or more of the following remedial actions:

8.13.9.2 Capillary columns-Turn off both oven and injection ports. Clean and deactivate the glass injector port insert or replace with a cleaned and deactivated insert. Remove the analytical column when the oven has cooled. Break off the first few inches of the column (up to one foot) on the injector port side and then reconnect the column. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

8.13.9.3 Metal Injector Port-Turn off the oven and injection port heaters and remove the analytical column when the oven and the injection port heaters have cooled. Remove the glass injection port insert (in instruments with off-column injection). Inspect the injection port and removed any noticeable foreign material.

8.13.9.3.1 Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone, toluene and then iso-octane, catching the rinsate in the beaker.

8.13.9.3.2 Use a solution of deactivating agent (Sylon-CT or its equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and reconnect the column.

8.13.10 Qualitative Analysis- Pesticides/PCBs

8.13.10.1 Identification of compounds by retention times must be performed by experienced gas chromatographers because slight shifts in retention times require judgment decisions. Observe retention time shifts of standards throughout a day's run to evaluate retention time shifts in samples. Utilize the daily retention time windows for compound identification. as a guide .

8.13.10.2 Confirm all compounds (pesticides/PCBs) on a second different column, or different detector (other than FID), unless the compound has been confirmed by GC/MS.

8.13.10.3 In performing 2 column confirmations it is important to also check the quantitated results from each column. A large quantitative difference is an indication of a possible interference. If the values differ by more than 40% the lower results should be reported and the “J” qualifier flag added to the data.

8.13.10.4 It is suggested that at least one sample from a set be confirmed by GC/MS, if compound concentration permits. It is the responsibility of the GC analyst to report any pesticides/PCBs confirmed by GC/MS. GC/MS confirmation is noted on the data sheet by adding the letter C to the amount of the compound being reported. For water samples, alpha-BHC, gamma-BHC, Endosulfan I and II, and Endrin must be confirmed on the pesticide extract rather than the BNA extract because these compounds are unstable at the basic pH.

8.13.10.5 Reporting Chlordane - Weathering and/or different formulations of chlordane may modify the technical chlordane pattern. If the chlordane pattern in a sample is similar ("similar" means all constituents are present, including heptachlor, in about the same ratio as a standard of technical chlordane) to technical chlordane, use a technical chlordane standard for quantitation. If the pattern is different but gamma and alpha chlordane and other chlordane constituents are present, use the individual chlordane constituent standards for calculation. Report the individual constituents on the data reporting sheet. Report a total of all constituents listed on the data sheet, except heptachlor, when the total is requested. Heptachlor is always reported as a separate constituent.

8.13.11 Calculation and Project Wrap-up -Pesticides/PCBs

8.13.11.1 The data package should contain the following information: GC Logbook number and page, project name, who calculated the data, who checked the calculation, when and who recorded the data and QC, and who verified and reported the data. The results of all QC calculations such as linearity check , % breakdown, calibration verification, and LCS, matrix and surrogate % recoveries should be included. The project verification form for both the primary and secondary analyst, the extraction sheet and the sample preparation report should also be included.

8.13.11.2 Individual chromatograms should contain information to identify the sample analyzed, volume and dilutions, and calculations used.

8.13.11.3 Do not erase or use "Liquid Paper" to correct any errors. Put one line (using ink) through the error with initials and date.

8.13.11.4 For calculation of components in a sample:

8.13.11.4.1 Prepare calibration standards at 5 concentration levels with a minimum of 3 for each compound of interest . However, for multi-peak compounds (e.g. technical chlordane, toxaphene, and the aroclors) a single concentration within $\pm$ 20 percent of the sample amount may be used. Calibration curves must meet the acceptance criteria specified in Method 8000B or in the specific analytical method being utilized. Qualify any results which did not meet specified calibration criteria. Refer to method specific SOPs for additional information on sample quantitation.

8.13.11.4.2 For samples with no analytes detected, calculate the MQLs based on the mass or volume of sample extracted, final extract volume, volume injected, dilutions (if any), and the lowest calibration standard analyzed. **MQLs for soils or sediments must be reported on a dry weight basis**

8.13.11.5 The following formulas are used for calculating sample concentrations:

Sample size factor (K):

$$K = \frac{\text{uL injected}}{\text{(Volume extract in uL) (dilution)}} \times \text{(mL, mg or gm extracted)}$$

For amount in sample:

$$\text{Concentration} = \frac{\text{Pk ht or area of sample}}{\text{Pk ht or area of std.}} \times \frac{\text{(ul inj)(conc.of std.,ng/ul)}}{K}$$

8.13.11.6 Calculation of off-scale peaks using peak height or area is allowable if it has been shown that response is linear in the concentration range of the off-scale peak and no interfering or rising baseline exists.

8.13.11.7 All data must be checked by the primary and secondary analyst. The chromatogram with the appropriate standards and QC showing the calculations for the reported data should be given to the secondary analyst. A hardcopy of the chromatogram should be placed in the project file.

8.13.11.8 The secondary analyst must check for accuracy of the transcription of data to the data report sheets.

8.13.11.9 Diluted samples and all standard vials used during analysis should be discarded at the completion of each project.

8.13.11.10 All vials that are ready for disposal should be placed in a waste safety can. Vials containing PCBs at concentrations greater than or equal to 50 ppm must be treated as hazardous waste and disposed of accordingly.

8.13.11.11 After analyses are complete all original sample extract vials should be stored in vial storage boxes in a refrigerator and placed in a secure area until disposal following appropriate procedures (See Chapter 4.)

8.13.11.12 The primary analyst is responsible for calculating surrogate, LCS, and matrix spike recoveries and recording the results on the appropriate data sheets and/or transmitting all results to the proper computer data system. Unusual results on QC data should be reported to a pesticide Lead Analyst, Section Chief, and Branch QA Officer. A hard copy of the recovery results must be included in the project file.

8.14 GC/MS Analysis - Volatile and Semivolatile Organic Compounds

8.14.1 GC/MS Logbook - Volatiles and Semivolatiles

8.14.1.1 Record all pertinent information requested on the logbook sheet. The electronic version of these forms are available on the Region 4 SESD's local network drive (K: drive) in appropriate subdirectories of K:\ASB\Forms\ or from the Branch QA Officer.

8.14.1.2 Record the GC/MS operating system file name under file name column.

8.14.2 GC Screen- Volatiles and Semivolatiles

8.14.2.1 Volatile Organic Compounds

8.14.2.1.1 Samples may be screened by headspace GC/MS to determine the approximate concentration level prior to GC/MS analysis. Dilutions for GC/MS analysis are to be determined from this screen analysis. The option of whether to screen samples is left to the analysts's discretion based upon information which is available at the time of analysis. This option is normally used for waste samples or environmental samples expected to contain high concentrations of analytes.

8.14.2.2 Semivolatile Organic Compounds

8.14.2.2.1 Samples may be screened by GC/FID, GC/ELCD, GC/PID, if necessary, to determine the approximate concentration level prior to GC/MS analysis. Dilutions for GC/MS analysis are to be determined from this screen analysis. The option of whether to screen GC samples is left to the analysts's discretion based upon information which is available at the time of analysis and is normally used for waste samples or environmental samples expected to contain high concentrations of analytes.

8.14.3 File Name Labeling- Volatiles and Semivolatiles

8.14.3.1 Use the following format for file names for volatile blanks and standards.

8.14.3.1.1 S0128R1 - R1 (or R2, R3, ect.) represents the standard run number, B for blanks, followed by date of ana lysis.

8.14.3.2 Use the following format for file names for semivolatile blanks.

8.14.3.2.1 <u>B00736SLW</u> "B" for blank, followed by 5 digit ASB log number for first sample in the set that standard applies to, followed by appropriate analysis designations. Some instrument software allows for only an 8 character file name.

8.14.3.3 Use the following format for file names for semivolatile surrogates and standards.

8.14.3.3.1 <u>S01997SLW</u> - Surrogate standard designation . "S" for standard, followed by 5 digit ASB log number for first sample in the set that standard applies to, followed by appropriate analysis designations, followed by the day of the month if the instrument software allows that length for file names. Some instrument software allows for only an 8 character file name.

8.14.3.3.2 <u>SA10726</u> - ."S" for standard, "A" for stock standard identifier code, "1" represents the first standard made from the stock, followed by the month and day of preparation. Surrogate compounds are normally included in the daily standard.

8.14.3.4 Use the following format for file names for samples

8.14.3.4.1 42361SLW - Use the ASB sample number followed by the proper analytical descriptor if the instrument allows that length for file names (i.e.).

8.14.3.5 Add the following designations between the SESD number and the analytical descriptor (i.e. 40849XDSLS):

8.14.3.5.1 X and Y - for duplicates.

8.14.3.5.2 D - Dilution (Indicate D2, D3, etc. for subsequent dilutions)

8.14.3.5.3 R, RS, R3, etc. - Designates a re-extraction of a sample or reinjection or a purging of a replicate VOA sample.

8.14.3.5.4 If other designations are needed, record their meaning in logbook.

8.14.3.5.5 NOTE: File names are limited to eight characters by some software currently in use.

8.14.4 Mass Scale Calibration Using FC43- Volatiles and Semivolatiles

8.14.4.1 Whenever a specific GC/MS system fails to meet the instrument performance tuning check the instrument must be mass calibrated. The following guidance may be used:

8.14.4.1.1 Admit FC43 with carrier flow entering source as appropriate for the individual instrument.

8.14.4.1.2 Adjust resolution to achieve the desired mass ratios as specified by the instrument manufacturer.

8.14.4.1.3 Make appropriate tuning adjustments to achieve the following ion intensity ratios as nearly as possible.

Mass 2l9 30-60% of Mass 69

Mass 220 $\geq$ Mass of 70

Mass 4l4 50-l25% of Mass 220 (for semi-volatiles)

Mass l3l ± 80-120%of Mass 2l9

8.14.4.1.4 Acquire at least 5 scans of FC43 ions scanning a mass range of 20-650 amu (20-550 amu for volatiles), or other appropriate mass range specified by the method.

8.14.4.2 Run calibration routine

8.14.4.2.1 Instrument should calibrate from at least 28 - 502 amu. Do not proceed until the appropriate masses are calibrated.

8.14.5 Instrument Tuning Performance Test- Volatiles and Semivolatiles

8.14.5.1 A tune performance check must be performed at a minimum of every 12 hours while performing sample analyses or as specified by the method..

8.14.5.2 Analyze 50 ng of Decafluorotriphenylphosphine (DFTPP) for semivolatiles or 50 ng of p-Bromofluorobenzene (BFB) for volatiles or the amount as required in the method (e.g. drinking water).

8.14.5.3 Other concentrations or compounds may be used as required by the analytical protocols.

8.14.5.4 Mass spectrometer operating parameters must be the same during the succeeding 12 hour sample analysis period as those used to obtain the most recent successful tune unless selected ion monitoring (SIM) is used.

8.14.5.5 The tuning standard must elute so that compounds of interest are resolved.

8.14.5.6 The mass spectrum must be acquired in the following manner unless the method specifies alternate criteria: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan within 10 scans prior to the beginning of elution of the performance compound.

8.14.5.7 Compare the ion intensity ratios to those in the tuning criteria of the appropriate method.

8.14.5.8 If the required tuning criteria are not met, the instrument must be returned until the spectra meets the specified criteria.

8.14.5.9 Check retention time and peak shape of the tuning compound to determine if they are consistent with prior results.

8.14.5.10 Check the peak intensity (by peak height or area) to determine if the sensitivity is adequate.

8.14.5.11 Print a list of masses and intensities, a copy of the chromatogram with areas of each peak printed, and maintain in the project file.

8.14.6 GC/MS Linearity Check- Volatiles and Semivolatiles

8.14.6.1 Initial Calibration - Volatiles and Semivolatiles

8.14.6.1.1 The GC/MS system must be initially calibrated with all compounds of interest at a minimum of five concentrations unless alternate criteria are specified by the method being used for analysis. Using the response factors (RF) from the initial calibration, calculate the percent relative standard deviations (% RSD) for all compounds.

8.14.6.1.2 A system performance check must be met for all compounds or as specified by the method. A minimum response factor of 0.05 for the volatile and semivolatile compounds is required. If this criteria is not met, corrective action must be taken.

8.14.6.1.3 The % RSD for each compound must be less than 15 percent unless alternate criteria are specified by the method being used for analysis. If this criteria is not met, corrective action must be taken. This might require instrument maintenance, new standards preparation, and/or repeating the analysis of the curve. If after corrective action some compounds exceed 15 percent RSD, the analyst may proceed, but any positive results for these compounds must be reported as estimated (qualified with a J flag).

8.14.6.1.4 It is acceptable to proceed with the analysis of samples if the %RSD for the following semivolatile compounds is less than or equal to (</=) 30%: 4-nitrophenol, 4-chloro-3-methylphenol, 2,4-dinitrophenol, 2-methyl,4,6-dinitrophenol, pentachlorophenol, 3,3-dichlorobenzidine, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline. It isacceptable to proceed with sample analysis if the %RSD is </= 30 % for the following volatile compounds: vinylchloride, 1,1-dichlorothene, chloroform, 1,2-dichloropropane, toluene, and ethylbenzene. If these analytes are of specific importance to the project, corrective action may be necessary to bring %RSD to </= 15%. These compounds must still be flagged as estimated (J) if the %RSD is greater than 15%.

8.14.6.1.5 The response factor (RF) for each compound at each concentration level of the calibration curve must be compared to the average RF of the curve to determine if any individual point on the curve is an outlier. Calculate the percent difference between the average response factor from the curve and the response factor from the individual concentration level in the curve. If the percent difference for any compound is greater than 20%, corrective action may be necessary. This usually requires re-analyzing the calibration standard whose RF exceeds the average RF of the calibration curve.

8.14.7 Continuing Calibration Verification- Volatiles and Semivolatiles

8.14.7.1 A standard mixture containing all volatile or semivolatile compounds of interest must be analyzed every l2 hours of operation or as specified by the method.

8.14.7.2 A system performance check must be met for all compounds or as specified by the method. A minimum response factor of 0.05 for the volatile and semivolatile compounds is required. If this criteria is not met, corrective action must be taken.

8.14.7.3 A calibration check of the initial calibration curve is made for each target compound. Calculate the percent difference between the average response factor from the initial calibration and the response factor from the daily calibration standard. If the percent difference (%D) of the initial RF and daily RF for any compound is greater than 20%, corrective action may be necessary. The analyst must immediately judge the impact on the data generated for that day. Any compounds with %D greater than 20% should be flagged as estimated (J). If more than 25% of the compounds are greater than 20%D, corrective action must be taken unless the analytical method in use specifies different criteria. This requires generation of a new curve unless the analyst can demonstrate and document that another type of corrective action has eliminated the erratic response factor.

$$\% \text{ Difference } (\%D) = \frac{RF_I - RFc}{RF_I} \quad X\ 100$$

RF_I - Average response factor for initial curve

RFc - Response factor from current standard mixture

8.14.7.3.1 Continuing without corrective action may be prudent if the outlier compounds are not of interest to the project. The Lead Analyst or Organic Section Chief must be consulted before continuing without corrective action. In this case, the corrective action may be to report these compounds as not analyzed or with an estimated flag.

8.14.7.3.2 For non routine analytes or special requests, in consultation with the data requestor , it is permissible to calibrate the instrument on the day of analysis with one calibration standard. The non-routine analyte may be quantitated against the one point calibration. Data points derived from a one point calibration must be reported as an estimated quantitation with the “J” flag assigned to the reported concentration. These types of calibrations must not be performed independently by the analyst, but shall only be performed after confirmation from the data requestor that a single point calibration will meet the project data quality objectives. Documentation of the project leader's acceptance of this type of data should be added to the project file

8.14.7.4 A file of the results from the initial and continuing calibration checks must be maintained. Continuing calibration files are part of the daily standard chromatograms and are to be filed with the appropriate project.

8.14.8 Analyze Standard Mixture- Volatiles and Semivolatiles

8.14.8.1 Analyze standard mixtures and performance compounds at least every 12 hours or as specified by the method (volatile standards should be at room temperature before analysis).

8.14.8.2 Use GC conditions and MS parameters consistent with sensitivity requirements and equal to those planned for the shift's operations.

8.14.8.3 Incorporate internal standards where feasible.

8.14.8.4 Perform system performance check and daily calibration check.

8.14.8.5 Record area count of the quantitation ion for the internal standards.

8.14.8.6 The surrogate standard is normally added to the BNA standard. A separate surrogate standard solution prepared by the extraction lab is also analyzed as a reference for calculating surrogate recoveries

8.14.9 Analyze Laboratory Blank- Volatiles and Semivolatiles

8.14.9.1 Utilize internal standards where required by the method.

8.14.9.2 Record integrations for the same internal standards recorded in the calibration standard.

8.14.9.2.1 If the area count is not within - 50% to + 100% of those in Standard Mixture, rerun.

8.14.9.2.2 Internal standard retention times must be within ±10 scans or 10 seconds of standard, whichever is greater.

8.14.9.3 Check for carryover from standard injection.

8.14.9.4 Compute surrogate recovery.

8.14.9.5 The Appendix to this Chapter gives further guidance on interpretation of blanks contaminants.

8.14.10 Analyze Samples- Volatiles and Semivolatiles

8.14.10.1 If area count of internal standard is not within - 50% to +100% of the standard, rerun the sample.

8.14.10.2 Internal standard retention times must be within ±10 scans or 30 seconds of standard, whichever is greater.

8.14.10.3 Intersperse field or lab blanks throughout the analytical run during the day as necessary.

8.14.10.4 Intersperse calibration standard mixtures between at a minimum of every l2 hours of analysis or as specified by the method.

8.14.10.5 Add internal standards as required by the method.

8.14.10.6 Compute surrogate recovery and record in GC/MS Log.

8.14.11 Drinking/Potable Water - Volatiles and Semivolatiles

Samples with positive results should be verified by analyzing a replicate sample whenever possible. The Lead Analyst or Organic Section Chief should be contacted if deviations from this policy are necessary.

8.14.12 TCLP analysis - Volatiles and Semivolatiles

The GC/MS data generated for VOA, BNA, and Pesticide analysis is reviewed with the Extraction Laboratory Chemist and a decision made whether any samples could fail the TCLP test based on the toxicity characteristic regulatory levels and the sample weight required for TCLP extraction (see EPA Method 1311, Section 1.2). If samples could potentially fail, then the TCLP extraction is performed and the analysis performed. If the sample cannot fail the test, this information is reported.

8.14.13 Qualitative Identification- Volatiles and Semivolatiles

8.14.13.1 Target compounds shall be identified by comparison of the sample compound mass spectrum to the mass spectrum of a calibration standard reference spectra. Two criteria must be satisfied to verify the identifications: (l) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample compound and standard compound mass spectra.

8.14.13.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within 12 hours of the sample. The RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

8.14.13.1.2 The requirements for qualitative verification by comparison of mass spectra are as follows:

8.14.13.1.2.1 All ions present in the standards mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. Target compounds present at low concentrations may not meet this criteria. The responsibility of reporting these compounds rests with the professional judgment of the Lead Analysts. Consultation with the QAO is encouraged.

8.14.13.1.2.2 The relative intensities of ions specified above must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

8.14.13.1.2.3 Ions greater than 10% intensity in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison.

8.14.14 Tentative Identifications- Volatiles and Semivolatiles

8.14.14.1 A library search shall be executed for non-target sample components for tentative identification. The most recent available version of the NIST and Wiley Mass Spectral Libraries should be used.

8.14.14.1.1 Do not report any compounds with a calculated value below the MQL. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

8.14.14.1.2 Guidelines for making tentative identification:

8.14.14.1.2.1 Relative intensities of major ions of the reference spectrum (ions greater than 10% intensity of the most abundant ion) should be present in the sample spectrum.

8.14.14.1.2.2 The relative intensities of the major ions should agree within $\pm$ 20%. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.

8.14.14.1.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

8.14.14.1.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

8.14.14.1.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination of coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.

8.14.14.1.2.6 If in the opinion of the mass spectral specialist, no valid tentative identification can be made, the compound should be reported as unidentified compound. The mass spectral specialist may give additional classification of the unknown compound, if possible (i.e. unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound).

8.14.14.1.2.7 Non-target compounds identified in samples will be reported using primarily the NIST, and as a secondary source the Wiley Libraries, to name the best probable match. The best probable match is selected by the mass spectroscopist from the best matches as chosen by the library search routine ranked by purity. The analysts interpretation may supersede the computer matching algorithm.

8.14.14.1.2.8 The NIST or Wiley Library nomenclature should be stripped of numbers or letters that would make the reported compound a specific isomer (e.g. 1,2-dibromoethane should be reported as dibromoethane).

8.14.14.1.2.9 Where more than one isomer of a compound is identified, they should be reported under one name. The total concentration should be reported with this one name and the number of isomers should be reported in parenthesis. The isomer name chosen for one sample of a project should be used in all samples for the project, where no distinguishable spectral differences are present (e.g. If the best match for C_3alkyl benzenes is methyl ethyl benzene instead of trimethyl benzene, or propyl benzene, report as methyl ethyl benzene in all samples of the project where this is true).

8.14.14.1.2.10 Name alkyl substituted analogs of target compound isomers using the earlier eluting of the isomers(e.g. methylfluoranthene, not methylpyrene).

8.14.14.2 Nomenclature for Library Search Compounds- Volatiles and Semivolatiles

8.14.14.2.1 Spaces in chemical names - Be careful where spaces are used in nomenclature especially when rearranging CAS names. Where there are dashes, always attach the words. Where there are spaces, always leave them.

8.14.14.2.2 Caution! Location of spaces, brackets, and parentheses are very important when entering names and should be entered consistently.

8.14.14.2.3 Names should be entered in all caps.

8.14.14.2.4 Isomers. Report as METHYLBIPHENYL (2 ISOMERS). Make sure spacing is strictly adhered to.

8.14.14.2.5 Isomers of Target Analytes: TRICHLOROBENZENE (NOT 1,2,4-) (2 ISOMERS).

8.14.14.2.6 Acids. Always precede acids with a space, same for esters, acetates, oxides, etc. (i.e. BENZOIC ACID).

8.14.14.2.7 Isomers and/or rearranged names, 2-HEXANONE, 5-METHYL-3-METHYLENE -, rearrange and combine to METHYLMETHYLENEHEXANONE. Dashes indicate no space when the name is rearranged.

8.14.14.2.8 Alkyls. No space.

8.14.14.2.9 Esters. Do not rearrange esters (i.e., DODECANOIC ACID, METHYL ESTER not METHYL ESTER OF DODECANOIC ACID).

8.14.14.2.10 Truncated names in data system. The current GC/MS data system library only stores the first 70 characters. Long names with odd looking endings should be looked up to verify the complete name. The HS library display truncates if the name extends beyond where the scan number is printed.

8.14.14.2.11 Unidentified compounds. Report as 5 UNIDENTIFIED COMPOUNDS, 5 equals the number of compounds.

8.14.14.2.12 Hydrocarbon series. Report homologous hydrocarbon series as "PETROLEUM PRODUCT" with an "N" flag in the result field.

8.14.14.2.13 Common names vs CAS names. The following commonly found compounds are changed from CAS names to common names:

2-PROPANONE TO ACETONE
2-PROPANOL TO ISOPROPANOL
2- BUTANONE TO METHYL ETHYL KETONE
2-PENTANONE TO METHYL PROPYL KETONE
3 METHYL-2-BUTANONE TO METHYL ISOPROPYL KETONE
4 METHYL-2-PENTANONE TO METHYL ISOBUTYL KETONE
THIOBISMETHANE TO METHYL SULFIDE
ACETIC ACID ETHYL ESTER TO ETHYL ACETATE
1,1'-OXYBISETHANE TO ETHYL ETHER
2,2'-OXYBISPROPANE TO ISOPROPYL ETHER
1,2-BENZENEDICARBOXYLIC ACID TO PHTHALIC ACID
ETHENYLBENZENE TO STYRENE

8.14.15 Quantitation of Compounds- Volatiles and Semivolatiles

8.14.15.1 Target components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The extracted ion current profile (EICP) area of characteristic ions of analytes are used. The average response factor (RF) from the initial calibration curve is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a response factor is calculated using the secondary ion.

8.14.15.2 Any compound that had a %RSD in RF of greater than 15 in the initial calibration curve must be reported with an estimated value flag (J). Similarly, any compound that had a % difference in RF of greater than 20 between the RF from daily standard mixture and the average RF from the initial curve must be reported with an estimated value flag (J).

8.14.15.3 An estimated concentration for non-target components tentatively identified shall be quantified by comparison to an internal standard free of interferences. The following order of preference for internal standards to use as a reference for semi-volatiles is D_{10}Phenanthrene, D_8Naphthalene, D_{10}Acenaphthylene, D_{12}Chrysene, D_{12}Perylene, and D_4 Dichlorobenzene. For volatile compounds, the internal standard nearest in retention time to the non-target compound which is free of interferences may be used to estimate concentration. Total area counts or peak heights from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A RF of one (l) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated to one significant figure for all tentatively identified compounds as well as those identified as unknowns.

8.14.15.4 The primary analyst is responsible for calculating surrogate lab control, and matrix spike recoveries and recording the results on the appropriate computer data sheet. Unusual results on QC data should be reported to the Lead Analyst and/or the Organic Section Chief. Primary and secondary analysts must complete the project data verification form.

8.14.16 GC/MS Data Transfer- Volatiles and Semivolatiles

8.14.16.1 Initial Reports - After the data is processed by the GC/MS data system, it is transferred to the laboratory information management system (R4LIMS). The data is then reduced taking into account sample dilution, amount purged or extracted, and dry weight, when applicable. Hard-copies are then produced. After corrections or additions are made to the data based on further analysis of the chromatograms and mass spectra, the final data product is transferred to the R4LIMS computer.

8.14.16.2 Final Reports

8.14.16.2.1 When data have been properly reviewed and checked by the primary and secondary analysts, the final data can be transferred to the R4LIMS system.

8.14.16.2.2 The data are then printed out in final production format and proofed for errors. Any corrections are made and the corrected data sheet is printed. A memo is also printed, the appropriate number of copies (include one file copy) are made and the report is signed by the project chemist and given to the Organic Section Chief for review.

8.14.17 Archiving Data

8.14.17.1 All samples and standards must be archived by copying to CD R or using other electronic storage devices.

8.14.18 Extract Handling

8.14.18.1 The GC/MS chemist is responsible for verifying that all sample extract vials were received from the extraction lab or GC analyst. The chemist is then responsible for the vials until GC/MS analysis is complete, and the vials have been stored or have been discarded. The extract vials should be stored in the refrigerator designated for semivolatile extracts when not in use.

8.14.18.2 Recap all vials that are to be retained as soon as possible after puncturing the septum. Remark the volume on the vial label after injection or dilution.

8.14.18.3 Diluted samples and standards should be discarded immediately following injection to avoid unnecessarily cluttering up the lab and extract boards.

8.14.18.4 All vials that are ready for disposal should be placed in the "Oily Waste Safety Can." Vials must be disposed of according to the procedures outlined in Section 4.6. Dispose of standard and sample vials containing PCB's and other listed compounds in a separate waste container.

8.14.18.5 Sample extracts are to be stored in storage containers after final reporting of data. These containers will be kept in their respective areas of the GC Lab and the GC/MS Lab in a refrigerator, based on the type of sample. As soon as possible after analysis, the containers should be disposed. Some criminal and other samples may need to be stored for extended periods of time. The sample storage custodian will furnish information on disposition of samples in a timely manner. All original sample vials are placed in boxes and are to be stored in a designated refrigerator upon completion of analysis until disposal.

8.14.19 GC/MS Files Storage- Volatiles and Semivolatiles

8.14.19.1 Chromatograms should be filed numerically according to sample numbers. Files should be labeled with the series of sample numbers on first line. Project name(s) should be listed under this. Chromatograms and each file should be arranged as follows:

8.14.19.1.1 Extraction sheets and data sheets.

8.14.19.1.2 Standards analyzed in order of date run.

8.14.19.1.3 Blanks analyzed in order of date run or sample # of blank series.

8.14.19.1.4 Samples analyzed in numerical order.

8.14.19.1.5 Pertinent GC screening chromatograms.

8.14.19.2 Any pesticides/PCBs confirmed by GC/MS must be reported to the pesticides Lead Analyst to be noted on the pesticide/PCB data sheet. Chromatograms from pesticide and PCB confirmation are sent to the GC unit to file with their chromatograms.

8.14.19.3 Keep GC screen chromatograms for samples that did not require GC/MS analysis.

8.15 Preparation, Storage, and Use of Organic Analytical Standards

8.15.1 Standard Sources

8.15.1.1 Primary Standards: Use commercial sources as available, request the grade appropriate to the analysis being performed . Consult the analytical method being used for standard purity.

8.15.1.1.1 Prepared standards: Order from commercial vendors with a known record of providing suitable standards.

8.15.1.1.2 Reference standards for verification of primary standards: must be ordered from a vendor other than primary standards whenever available.

8.15.1.1.3 Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source. If the purity of these standards is questionable, report the data based on these standards as estimated.

8.15.2 Glassware, Equipment, and Solvents Needed to Prepare Standards:

8.15.2.1 Analytical balance, capable of an accuracy of $\pm$ 0.1 mg.

8.15.2.2 Spatula, stainless steel.

8.15.2.3 Transfer class "A" pipettes and Pasteur disposable pipettes or suitable syringes.

8.15.2.4 Flasks, volumetric, 25, 50, 100 and 200 mL.

8.15.2.5 Bottles, Teflon®-lined caps 60 mL.

8.15.2.6 Small glass funnels, and bent paper clip.

8.15.2.7 Refrigerator.

8.15.2.8 Pesticide grade solvents: ethyl acetate, toluene, acetone, isooctane, hexane, methanol, and carbon disulfide.

8.15.3 Safety Precautions and Operating Procedures

8.15.3.1 Gloves should be used when handling standard materials.

8.15.3.2 Standards used for quantitating samples are to be made by a chemist.

8.15.3.3 Hoods should be used when weighing toxic standards or diluting with organic solvents.

8.15.3.4 Rinse all glassware prior to use with methanol, acetone, and isooctane and let air dry in hood.

8.15.3.5 Perform a balance check with Class-S weights each day the balance is used. Record the balance check in the appropriate logbook. A secondary analyst must check calculations for standard solutions which are being prepared prior to the actual addition of standard material to the solvent.

8.15.3.6 Do not store any standards in volumetric glassware. Transfer to a 60-mL screwcap bottle with Teflon® liner if the solution is to be stored. Use phosphate tubes or vials, with Teflon® liners, for short term storage. All standards must be properly labeled.

8.15.3.7 Always rinse used glassware with acetone before washing in dishwasher with other glassware. Rinse pipettes out with acetone immediately after use.

8.15.3.8 Keep all standards in refrigerator or freezer when not in use.

8.15.3.9 Always let standards and solutions come to room temperature before opening.

8.15.3.10 Check new working standard against old standard. The old standard may be slightly more concentrated due to evaporation of solvent from repeated openings.

8.15.3.11 Transfer waste standards to a waste bottle. Rinse the empty bottle several times with acetone. Add the rinsate to the waste bottle and discard the standard bottle.

8.15.3.12 Provide a large waste beaker located in a hood for rinsing all used glassware and pipettes before washing with soap and water. Transfer the wash solvent to a waste bottle.

8.15.3.13 Volumetric flasks and storage bottles used for standards must be rinsed several times with distilled water to remove any alkaline residue. Alkaline residues cause degradation of certain organics and pesticides.

8.15.4 Standards

8.15.4.1 New working standards must be checked against the old working standards prior to use. The evaluation criteria are: (1) 75 percent of the analytes in the new working standard must be within $\pm$10 percent of the old working standard and (2) for any analyte in the new working standard that is equal to or greater than $\pm$ 25 percent of the old working standard professional judgement shall be used to complete the evaluation. In these cases consultation with the OCS Chief and ASB QAO is required and all decisions must be properly documented. The new working standard must also be compared to the check standard on a quarterly basis or any time a new calibration curve is developed. The Lead Analyst shall use the same criteria for evaluating the working standard versus the check standard that is used for comparing the old and new working standards. The schedule for discarding working standards shall be at the discretion of the Lead Analysts and based on professional judgement and/or check standard results. In all cases standards shall be discarded at the manufacturers expiration date.

8.15.4.2 Pesticide/PCB standards - Replace stock standards and "non-working" standards at a minimum of annually. More frequent replacement may be required if specified by the analytical method. Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions

8.15.4.2.1 Suggested procedures for preparation of stock standards follow (also consult procedures found in SW-846 methods or other method being utilized for the analysis).

8.15.4.2.2 Weigh 50.0 mg of primary standard into a beaker using a small spatula for solids or a disposable Pasteur pipette for liquids. It may be necessary to aid dissolution by adding as small amount of solvent (e.g. ethyl acetate or toluene).

8.15.4.2.2.1 Some standards may require placing the beaker in an ultrasonic cleaning device or on a steam bath for complete dissolution.

8.15.4.2.3 Transfer through a glass funnel into a volumetric flask, washing with an appropriate solvent. Dilute to volume with the least volatile of the appropriate solvents and mix. Calculate the concentration in micrograms per microliter. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. If the purity is less than 96%, the weight must be adjusted for purity.

8.15.4.2.4 Transfer to a screw capped bottle. Old bottles that contain the same standard may be reused if rinsed with isooctane.

8.15.4.2.5 Calibration Standards - This normally consists of a set of five standards with concentrations covering the linear range for each detector used for quantitative analysis.

8.15.4.2.6 Intermediate and working standards, are diluted with a high boiling solvent such as isooctane. Working standards are diluted from intermediate and working standards to give even numbered concentrations if possible, (i.e. 10 ng/uL vs 11 ng/uL).

8.15.4.2.7 All standards must be stored in refrigerator when not in use.

8.15.4.2.8 Surrogate and Matrix Spike Solution - All spike solutions are made from stock or intermediate solutions and diluted with acetone or methanol.

8.15.4.3 Volatile standard solutions- Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

8.15.4.3.1 Place about 9.8 mL of methanol into a 10 mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.l mg.

8.15.4.3.2 Add the assayed reference materials as described below:

8.15.4.3.2.1 Liquids - Using a 100 uL syringe, immediately add 2 or more drops of assayed reference material to the flask, then re-weigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

8.15.4.3.2.2 Gases - Introduced from lecture bottle. Flow rate is controlled with a valve through a Teflon® tube to top of the meniscus.

8.15.4.3.3 Re-weigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

8.15.4.3.4 Transfer the stock standard solution into a Teflon® sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

8.15.4.3.5 When stored under the above conditions, those standards should be replaced if comparison with QC check samples indicates a problem. Gases are replaced after 3 months and all others after 6 months.

8.15.4.3.6 Intermediate standards - Using stock standard solutions, prepare intermediate standards in methanol that contain the compounds of interest, either singly or mixed together. The intermediate standards should be prepared at concentrations such that the aqueous calibration standards will bracket the working range of analytical system. Intermediate standards should be diluted to give calibration standards of approximately 30 ng/uL.

8.15.4.3.7 Intermediate standards are prepared as needed and should be stored in a freezer with minimal headspace. They should be checked frequently for signs of degradation or evaporation, especially prior to preparation of calibration standards.

8.15.4.3.8 Internal/Surrogate standard spiking solution - The solution may be prepared as described above or with a dilution of a commercial standard. The intermediate surrogate solution is prepared as needed. The stock standard is good for a minimum of 6 months. The first compound is a good barometer of the solution; if it appears to be much smaller in size than the other two in a GC/MS run, the stock solution should be discarded and another one made.

8.15.4.4 Semivolatile standard solutions- Purchase stock standard mixtures from a certified vendor at 2000 ng/ul concentrations for each component. Prepare standards as follows:

8.15.4.4.1 Intermediate standard -The intermediate standard should be prepared at least once per year. Allow standards to warm to room temperature and sonicate a few minutes before next step. Add 500 ul of each standard mixture to 10 ml volumetric flask and dilute to mark with methylene chloride to make the intermediate standard. Label the first standard in this series BNA-SA. The next intermediate standard made will be labeled BNA-SB etc. This will make it possible to trace any analysis back to a specific analytical standard..

8.15.4.4.1.1 A standard from a different certified vendor is prepared at the same concentration for a check standard. This standard is used to check the integrity of the primary analytical standard.

8.15.4.4.2 Working standard - The working standard is made by adding 400 ul of the intermediate standard, 50ul of surrogate standard obtained from the extraction lab, and 10 ul of internal standard to 550 ul of methylene chloride. The first working standard made from the intermediate standard (BNA-A) will be labeled BNA-A1, the second BNA-A2, etc., until the standard is used up or a new standard is made. Other concentrations are prepared as needed.

8.15.4.4.3 Internal Standard Preparation - Purchase a stock internal standard mixture from a certified vendor with each component at a concentration of 4000 ng/ul. The stock standard is diluted 1 volume of standard to 3 volumes of methylene chloride to give a concentration of 1000 ng/ul for the spiking standard.

8.15.5 Calibration Standard Records

8.15.5.1 Stock Standards. Enter the weight of the primary standard and other requested information on the stock standard sheet in the Quality Control Standards Logbook. Also, record the requested information on the summary log sheet at the beginning of the section, and on the label of the standard bottle.

8.15.5.2 All logbook pages and forms can be found on the Region 4 SESD’s local network drive (K: drive) in appropriate subdirectories of K:\ASB\Forms\ .

8.15.5.3 Each stock solution is assigned a discrete number that identifies that particular stock solution. Whenever a new stock solution of the same compound is made up, the original number should be retained.

8.15.5.4 Record the standard identifier code, dilution number and date of preparation on the standard sheet.

8.15.5.5 A new standard sheet must be prepared when one or more ingredients or the concentrations in a mixture changes. Retain the old mix bottle number on the new mix. Select a new number when a completely new mix or standard is made up. Retire the number when a mix or standard is no longer needed.

8.15.5.6 In GC and GC/MS Logbook, enter name of the standard plus the identifier code.